DISCOVERY OF DIOXIN CONTAMINATION IN THE WOONASQUATUCKET RIVER. A PRELIMINARY STUDY OF THE CENTERDALE MANOR RESTORATION PROJECT SUPERFUND SITE, NORTH PROVIDENCE, RHODE ISLAND, USA

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Introduction

When high concentrations of heavy metals were found in fish from the Woonasquatucket River and Southeast Asian American (SEAA) fishermen were reportedly subsistence fishing in the river, EPA initiated an investigation. T he results of that investigation of metals, pesticides, polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PC DDs) a nd diben zofurans (P CDFs) in sunfish and eels (fillets and offal) showed unacceptable levels of PCDDs and P CBs . In particular, very high con centrations o f the toxic PC DD co ngener, 2,3 ,7,8-tetrachlo rodiben zo-p-diox in (2,3,7,8-TCDD), were detec ted. The d iscovery pro mpted an investigation o f 2,3,7,8-TCDD in sediments b ehind seven dams alon g the river. T his PCD D conge ner was sub sequently foun d in high concentrations in the sediments behind all the dams, except one, the most northern dam. Highest concentrations were found in two impoundments near historic mill sites. An unknown peak later identified as 1,2,4,5,7,8-hexachloroxanthene (HCX)was also detected in the sediments of the river. The fact that 2,3,7,8-TCDD was found along with HCX was an indicator that the manufacture of the antibacterial pesticide hexachlorophene could be the source of the contamination. Behind the first river dam sampled, neither 2,3,7,8-TCDD and HCX were detected in the sediments. The sediments behind the second dam contained very high concentrations of both compounds and the levels then decreased with distance down the river. The discovery of 2,3,7,8-TCDD and HCX in sediment adjacent to a site originally used as a chemical manufacturing plant led to the discovery o f high concen trations of PC DDs in so ils and subseq uently led to a full scale Comprehensive Environmental Response, Compensation and Liability act (CERCLA) investigation o f the site, river and p ond sedim ents and ad jacent wetlands.

History

In May of 1994, Haley Wurzel, Vanessa Tomasic, and Kelley Park of Brown University collected sediment sa mples in the W oonasq uatucket Riv er RI at the V alley Street D am and fo und high leve ls of heavy me tals. In May o f 1995, S iemay Lee o f Brown U niversity wrote “A re Turne r Reservo ir Fish safe to Eat? A risk Assessm ent of Rhode Island S outheast Asian American (SEAA) Fishers” and also found high levels of heavy metals in fish. Indira Balkinsoon of EPA Region 1 and RI DEP officials recognized this fact and as part of the EPA Urban E nvironmental Initiative and Rhode Island Gre enway Pro ject initiated a stud y of fish in the W oonasq uatucket Riv er. A sampling p rogram w as designed to investigate tho se areas whe re SEAA fishers were be lieved to catch fish for consumption. Further inform ation about the SEA A fisherman indicated that the fish were prepared by frying the complete fish further causing possibly higher human health risk.

Organohalogen Compounds, Volumes 60-65, Dioxin 2003 Boston, MA

Initial investigation

Hook and line sampling resulted in the collection of sunfish (Centrachidae) and Am erican eels (Angu illa rostrata). Sampling was conducted on 1 June 1996. Sunfish were collected from the Valley Stree t impound ment and e els were colle cted near a n old mill race way adjac ent to Allend ale Pond. Three sunfish muscle fillet and offal composites and two eel fillet and offal composites were analyzed. The fish were processed and analyzed at the EPA Narragansett laboratory (AED)

facility. Samples were analyzed for mercury, cadmium, copper, nickel, chromium, lead and zinc as well as DDT , DDE, D DD, chlorda ne, transnonchlor, NO AA list PCBs, and PCDD s and PCD Fs. The laborato ry detected significant amounts of 2,3,7,8-TCDD and dioxin-like PCB s. Concentrations ranging between 17 pg/g and 554 pg/g wet weight of 2,3,7,8-TCDD were measured in the fillet and offal sam ples. Regio n 1 EPA needed to confirm A ED LRGC/M S results with Region 7 HRGC /HRMS data that could be used for risk assessment. The extracts from AED were sent for analysis and the data indicated that the results were comparable. In September 1996, the EPA R egion 7 lab oratory (R -7) confirme d the AE D screen ing result with meth od 161 3 results validated b y Region 1 . The com parisons ar e as follows: Su nfish TCD D-63.1 ppt (AE D) vs 41 .0 ppt (R-7) : Eel TCDD - 91.7 ppt (AED) vs. 85.8 ppt (R-7). Using the above results, a risk screen was perfor med in Se ptember 1996 a nd the scree n indicated th at 95% of the risk was fro m 2,3,7,8 TCDD and 5% from PCB . This discovery prompted EPA to pursue further investigations in the impound ment sedim ents behind all the dams alo ng the W oonasq uatucket Riv er.

Sediment Investigation

In October 1997, seven surface sediment samples were collected directly behind each of the seven impoundment dams on the Woonasquatucket River from Centerdale to North Providence. Figure 1 depicts the sampling locations and concentrations (pg/g=ppt) of 2,3,7,8-TCDD and 1,2,4,5,7,8-hexachloro-(9H)xanthene (HCX). The levels of 2,3,7,8-TCD D detected were considered very high compa red to the 1 .0 ppb TCDD nominal Su perfund cle an-up level (2).

Initially chemists at AED using full scan low resolution gas chromatography discovered a non dioxin peak and tentatively identified the peak as HCX. The presence of this compound was later confirmed by EPA Region 7. This discovery let to speculation that the presence of 2,3,7,8-TCDD along with H CX was a result of the ma nufacture of he xachloro phene from 2,4,5-trichlo ropheno l (4). Similar discoveries were documented by EPA Region 7 chemists during the investigation of the Times Beach Sup erfund sites in M issouri. The origin of the M issouri contam ination was fou nd to be the manufacture of 2,4,5-trichorophenol, 2,4,5-TP Silvex, and hexachlorophene (1).

Figure 1. Concentrations of 2,3,7,8-TCDD and 1,2,4,5,7,8-hexachloroxanthene in sediments from the Woonasquatucket River.

Based on the sediment data (Figure 1) it was presumed that the TCDD/ HCX may have originated from a chemical manufacturing facility near or on the river below the Esmond dam, where very little 2,3,7,8 TCDD was found, and the Allendale and Lymonsville Dams, where high concentrations were measured. Historical records indicated a mill located on Centerdale Manor property along the shore of the Woonasquatucket River and adjacent to Allendale Pond. The original mill was destroyed in the Mid 70's by fire and was replaced in the Mid 80's by two apartment/condominium buildings. The initial site investigation results for the property did not include the an alysis of PCD Ds/PC DFs. Furth er investigation also indicated that when the m ill closed for th e produ ction of cloth it wa s converted into a chemic al manufactu ring facility.

In September 1998, EPA collected 45 soils and sediment samples at the Centerdale property. The results of those samples indicated 4 parts per billion TCDD in Centerdale soils and 14 ppb along the river bank.(3).

Soil investigations

Due to the discovery of the high levels of predominately 2,3,7,8-TCDD, EPA initiated further investigations on the Centerdale property and the adjacent wetlands and residences. Concentrations on the Centerdale Manor property were found as high as 140 ppb. Shore line sediments along the Woonasquatucket River were found up to 8 ppb 2,3,7,8-TCDD near homes and athletic fields that bordered A llendale and Lymonsv ille Ponds.

These results prompted EPA to perform several time critical investigations on affected properties and later non-time critical stabilization of the shoreline and wetlands sections to prevent further erosion of contaminated soils.

Chemical contamination origins

Further investigation of the chemical manufacturing practices at the site indicated that the chemical compa ny started to p roduce h exachlorp hene by the re action of 2,4 ,5-trichorop henol with formaldehyde during the 1960's. By-products of this process include HCX and 2,3,7,8-TCDD. The ratio of TCD D and H CX from soil samples c ollected in 1 998-99 at the site was ap proxima tely 1, 2,3,7,8-TCDD, to 20 HCX. This ratio is indicative of the manufacture of hexachlorophene from 2,4,5-trichlo ropheno l and not the m anufacture o f 2,4,5-trichlor opheno l as the initial reactan t. Several other sites in the US are contaminated with 2,3,7,8-TCDD and o ther PCDD congeners due to the manufacture of 2,4,5-triclorophenol from tetrachlorobenzene (4). It is well known that between 1960 and 1970 the production of 2,4,5-trichorophenol without 2,3,7,8-TCDD contamination was very difficult. Many clea n-up steps need to be em ployed to prod uce a colorless, dioxin free 2 ,4,5-trichoro phenol.

The toxicity of 2,3,7,8-TCDD is well known, but the toxicity of HCX is not well characterized at this time but has been estimated in later EPA work that will be discussed in future papers.

Discussion:
Thus, from a small sampling of fish from the Woonasquatucket River to study risks to SEAA fishers, indications of significant environmental contamination were discovered. The discovery of 2,3,7,8-TCDD and HCX and the use of 2,3,7,8-TCDD/HCX ratios proved an important indicator of site specific dioxin contamination. This helped to pin down where the chemicals were manufactured, by whom, and for what purposes. Previous information from the Region 7 2,3,7,8-TCDD/HCX research was critical in helping to determine the contamination source.

Disclaimer: Although the information in this document has been funded wholly by the USEPA it does not necessarily reflect the views of the agency and is no official endorsement should be inferred.

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